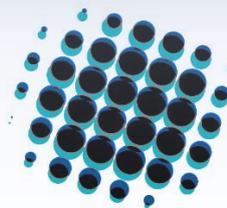


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Application Note: Analysis of Varnish

Background and Approach

When performing building or art restoration, experts often need to understand the origin and nature of a varnish coating. This knowledge can aid future conservation by allowing the restorer to use similar materials, or enabling them to use appropriate removal strategies. Key characteristics that are typically of interest to conservators are the origin of the oil, e.g. linseed, and whether or not the oil is heat-treated. We can determine both of these features by chemically treating the varnish of interest and analyzing the products by gas chromatographic separation followed by mass spectrometry detection (GC-MS).

Initially, a small subsample of the varnish is hydrolysed it into its constituent fatty acids and these are then methylated immediately prior to GC-MS analysis to allow detection. From the resulting fatty acid distribution we can determine whether the source of the oil and whether it has been pre-treated. In the experiment described herein, two different varnish samples from different fine art exhibits were analysed.



Methodologies

Sample Preparation

The reagent (trifluoromethylphenyl)-trimethylammonium hydroxide (TFTMTH) was used to carry out hydrolysis / methylation of varnish samples following published methods e.g. (Sutherland,

2001, 2007; Piccirillo, Scalarone and Chiantore, 2005; Tammekivi et al., 2019). Sub samples of varnish (~1mg) were initially placed in 20 µl TFTMTH in a 1.5 ml Eppendorf tube and left to react overnight at room temperature. In an attempt to drive the hydrolysis to completion, a further 20 µl of TFTMTH was added the following day and the Eppendorf tubes placed at 60 °C for 2.5 hours. A 1-2 µl aliquot of each digested sample was taken for analysis. Duplicate blank samples (TFTMTH only) were prepared and processed as per the varnish samples.

Gas Chromatography – Mass Spectrometry

All analyses were performed by use of a TSQ Duo Trace 1300 GC-MS (Thermo Scientific) instrument. The initial GC oven temperature was 50 °C which was held for 2 mins followed by a temperature ramp at 4 °C/ min to a final temperature of 280 °C which was held for 5 minutes. Helium flow was 1 ml/min and a split ratio ranging from 20:1 to 100:1 was used. A 5 % phenyl methyl polysiloxane GC column was used (HP-5MS, 30 m x 0.25 mm x 0.25 µm, Agilent). The GC inlet temperature was 280 °C and the MS transfer line was also maintained at 280 °C with the ion source temperature at 230 °C. Electron impact ionisation was performed at 70 eV. Peaks of interest were



Figure 1. Our Thermo TSQ Duo GC-MS/MS instrument is equipped with adaptors for small and large vials and an autosampler that can inject gaseous (head space), liquid or SPME fibres for concentrating volatile samples.

identified and peak areas determined to calculate ratios of sample components. All results were corrected using the TFTMTH blank samples and an average of the replicate samples used. Chromatograms were processed using Chromeleon software (v7.2, Thermo Scientific).

Findings

Confirmation of Sample Type

Azelate, palmitate and stearate were all present in both samples tested indicating the presence of an oil (Figure 2). In addition the azelate peak was of similar magnitude to that of palmitate further indicating the presence of oil, as opposed to an egg tempera media for example (Mills and White, 2003), which shows rather different ratios of azelate to palmitate.

Heat Treated vs. Raw

The azelate to suberate and sebacate ratios are indicative of whether the oil is pre-polymerised (heat-treated) or has been used raw. Sample A had an azelate : suberate ratio of 1.8 and an azelate : sebacate ratio of 6.4 (Table 1) which is consistent with a heat treated oil (Mills and

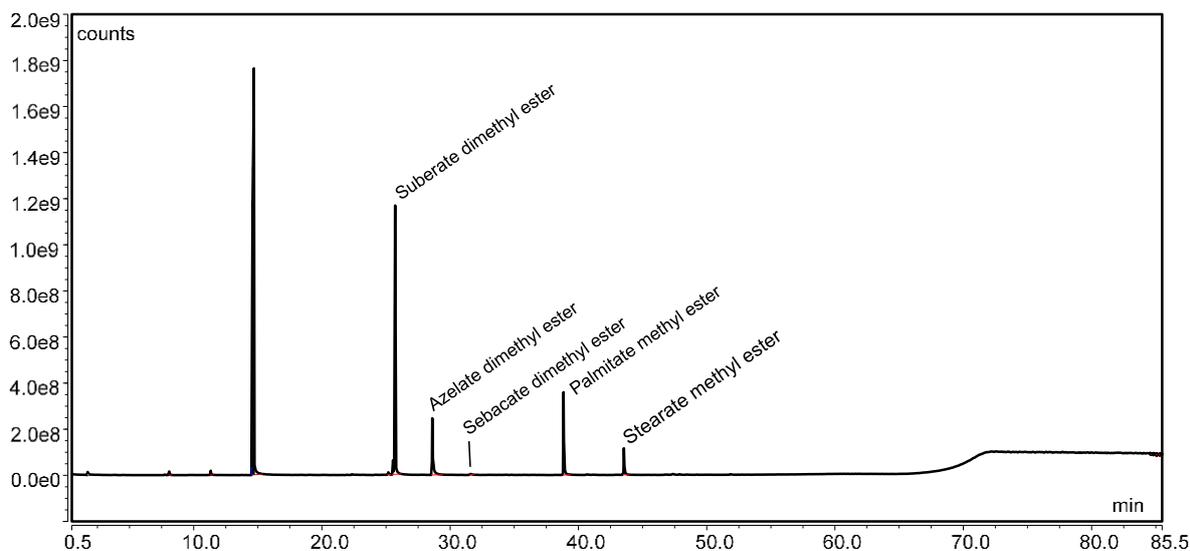


Figure 2. Example chromatogram obtained from varnish sample following GC-MS analysis. Peaks are shown for the methyl esters of palmitate, stearate, azelate, suberate and sebacate .

<i>Sample</i>	<i>P/S</i>	<i>A/Sub</i>	<i>A/Seb</i>
<i>Sample A</i>	<i>1.4</i>	<i>1.8</i>	<i>6.5</i>
<i>Sample B</i>	<i>3.1</i>	<i>6.4</i>	<i>25.0</i>

Table 2. Ratios of different components present in the varnish samples analysed. P = palmitate; S = stearate; A = azelate; Sub = suberate; Seb = sebecate.

White, 1982). Conversely, sample B had an azelate : suberate ratio of 6.4 and an azelate : sebacate ratio of 25.0 consistent with a raw oil (Table 2) (Mills and White, 1982).

Source of Drying Oil

The palmitate : stearate (P/S) ratio is indicative of the oil source (Mills and White, 2003). In the present study, varnish sample A had a P/S ratio of 1.4 which is consistent with the oil being derived from linseed whilst sample B had a P/S ratio of 3.1, consistent with a poppy seed derived oil (Mills and White, 2003).

Summary

After digestion of the varnish, mass spectrometric analysis was performed following gas chromatography (GC-MS) to separate and identify the components present. The analysis revealed Sample A to be derived from a heat-treated linseed oil whilst Sample B was derived from raw poppy seed oil.

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